

Effect of plasma power on degradation of chitosan

Kwang-Rae Lee^{*,†} and Kun-Ho Song^{**}

^{*}Department of Chemical Engineering, Kangwon National University,
192-1, Hyoja-dong, Chuncheon, Gangwon-do 200-701, Korea

^{**}Gangwon Institute for Regional Program Evaluation, 192-1, Hyoja-dong, Chuncheon, Gangwon-do 200-701, Korea

(Received 30 June 2013 • accepted 20 October 2013)

Abstract—The depolymerization of chitosan by plasma in the presence of oxygen (O₂) and nitrogen (N₂) was investigated with various PECVD power. The degree of the depolymerization was determined by measuring the viscosity. With 100 W of PECVD, the average molecular weight (M_w) decreased from 93,000 of raw chitosan to about 41,000 with plasma-treating time of 5 min in N₂, and 45,000 in O₂. The depolymerization of chitosan increased with increasing PECVD power from 100 W to 400 W, and with increasing PECVD treating time from 1 min to 5 min. FT-IR showed the absorption band peaks of the amine (-NH) band at 1,541-1,549 cm⁻¹ and the carbonyl (C=O) band at 1,654 cm⁻¹ and 3,422-3,488 cm⁻¹ substantially decreased. The decrease in band peaks means that the chain of chitosan macromolecules was broken into smaller unit which results in decreasing viscosity. Therefore, plasma treatment in the presence of O₂ or N₂ is a potentially applicable technique for the production of low molecular chitosan.

Keywords: Chitosan, PECVD, Plasma, Molecular Weight

INTRODUCTION

Chitosan is one of the most abundant natural biopolymers. The reaction of chitosan is more versatile than cellulose due to the presence of NH₂ groups. It has been studied extensively for various applications such as food additives, artificial skins, wastewater treatment where the removal of heavy metal ions by chitosan through chelation [1-3]. Studies on chitosan composites have also focused on its strong antimicrobial activity and biocompatibility. Nylon-6/chitosan composites were shown as candidate for antibacterial agents [4]. The association of chitosan and bioactive glass matrix promotes a highly significant bioactivity, demonstrating surface bone formation and satisfactory behavior in biological environment [5].

Recently it was reported that the bacterial cellulose/chitosan composites significantly improved physico-chemical and mechanical properties compared to pure bacterial cellulose and would be suitable for wound dressing and other biomedical applications [6].

Chitosan is only soluble in aqueous solution of some acids, and some selective N-alkylidinations [1,7]. Although several water-soluble derivatives are obtained [8], it is difficult to develop solubility in common organic solvents by these methods. Modification of the chemical structure of chitosan to improve the solubility has been attempted, but only few of the derivatives of chitosan are found to dissolve in conventional organic solvents [9-12]. Due to its physical and chemical properties, chitosan is being used in widely different products and applications. Different applications require different properties of chitosan. These properties change with degree of acetylation of chitin and molecular weight as well. The molecular weight control of chitosan has been attempted as well as the modification

of the chemical structure of chitosan. The various applications were very strongly dependent on the molecular weight of chitosan. For proper applications, an appropriate molecular weight control of chitosan is necessary. There have been two ways for depolymerizing the chitosan [13,14]: chemical and enzymatic methods. The chemical methods involve hydrolysis of chitosan using acids. The others are enzymatic methods. The chemical methods have inherent drawbacks, which are unsuitable for products toward human uptake, and the enzymatic methods have a relatively low productivity.

To avoid the problems of the chemical hydrolysis and the enzymatic methods, the plasma generated by PECVD was employed in this study to cut the molecular weight of chitosan for obtaining the less molecular weight one.

EXPERIMENTAL

1. Chemicals and Equipment

For plasma generation, PECVD (Plasma-enhanced chemical vapor deposition) device was manufactured by SNTek (Korea); the frequency of its RF-Generator was 13.56 MHz. RF power range was 10-600 W. RF impedance was 50 ohm nominal. O₂ and N₂ gases were used as the processing gas of the device. Acetic acid (1% w/w) for dissolving chitosan flake was purchased from Junsei, toluidine blue powder from Sigma-Aldrich, PVSK solution (N/400 Potassium Polyvinyl Sulfate Titration Solution, C₂H₅OSK) from Wako (Osaka, Japan), Chitosan flake of 60 mesh from Youngchipharm (Korea).

2. Method

Plasma treatment: Chitosan flake of 3 g was plasma-treated in PECVD chamber filled with N₂ and O₂ gases for 1, 2, 3, 4, 5 minutes with increasing the power by 100 W in the range of 100 W-400 W.

Viscosity measurement: The plasma-treated chitosan of 0.2 g was solved in the aqueous acetic acid solution of 1.0 w/w%. The relative viscosity of the solution was measured using Brookfield viscome-

[†]To whom correspondence should be addressed.

E-mail: krlee@kangwon.ac.kr

Copyright by The Korean Institute of Chemical Engineers.

ter (DV-1 prime) with spindle SC4-18 at 25 °C in the range of 30-60 rpm.

FT-IR spectrum: KBr pellet was fabricated with the mixture of plasma-treated chitosan and KBr powder and FT-IR (BIO-RAD, Excalibur, USA) was used to identify the decrease in absorption band peaks.

RESULTS AND DISCUSSION

1. The Color Change

The color of the chitosan powder treated with plasma was observed with the naked eye. The color of the chitosan powder was changed from white to brown with increasing PECVD power and time treated with plasma. Both the processing gases of O₂ and N₂ showed similar trend of color change. However, the color change in case of the processing gas of O₂ was more drastic and observable than in case of N₂; the color changed under the power of 300 W in processing gas of O₂, however under the power of 400 W in N₂. Chitosan was more vulnerable in color change with the processing gas of O₂ than N₂.

2. Degree of Deacetylation (DD)

DD was calculated using the equation described in Eq. (1) [15]. To obtain DD by the colloid titration method, 5 g of chitosan which was dried in drying oven for 3 hr at 105-110 °C was solved in 300 mL of 1.0 wt% acetic acid aqueous solution. After passing through filter paper (Whatman No. 4), 1.0 g of the filtered chitosan solution was titrated with the PVSK solution. Aqueous solution of 0.1 wt% toluidine blue was used as indicator. The color changed from blue to red-purple at the end-point of titration

$$DD(\%) = \frac{X/161}{X/161 + Y/203} \times 100 \quad (1)$$

$$X = \frac{1}{400} \times \frac{1}{1000} \times f \times 161 \times V \quad (2)$$

$$Y = 0.5 \times \frac{1}{100} - X \quad (3)$$

where V: the amount of 1/400 N (2.5 mN) PVSK consumed in titration (mL)

f: normal concentration coefficient of 1/400 N (2.5 mN)

161 : molecular weight of chitosan unit

203 : molecular weight of chitin unit

The calculated DD based on the viscosity measured at various powers of PECVD and plasma-treating time is shown in Tables 1 and 2; DD was above about 96% in the processing gas of both O₂ and N₂.

3. The Viscosity of the Chitosan Flake Treated with Plasma

The viscosity and molecular weight of chitosan are affected by the size of chitosan molecule. The viscosity of the plasma-treated chitosan solution was measured to obtain the molecular weight of chitosan. The chitosan powder treated with plasma at various PECVD power and the processing gases (O₂, N₂) was solubilized with aqueous acetic acid as described above and the viscosity of the solution was measured at 20 °C using a Brookfield viscometer (DV-II). As shown in Tables 1 and 2; at 100 W, the viscosity was decreased with plasma-treating time from 115.2 cp of raw chitosan to about 73 cp. The decrease in viscosity means that the chains of chitosan molecules were broken by the plasma. Above 200 W, however, the viscosity did not depend on plasma-treating time, which means that the plasma-treating time above a certain energy did not affect the molecular structure.

4. Molecular Weight of the Chitosan Treated with Plasma

The molecular weight (M_w) of the plasma-treated chitosan was

Table 1. Viscosity, DD(%) and Mw of plasma-treated chitosan in N₂

Gas	Power (W)	Plasma treating time (min)	Viscosity [η] (exp.)	Degree of deacetylation (DD%) (cal.)	The molecular weight (Mw) (cal.)
N ₂	100	1	96.01	95.89	59,000
		2	88.94	96.68	52,000
		3	86.27	94.42	51,000
		4	83.21	96.62	49,000
		5	73.9	97.14	41,000
	200	1	67.87	97.41	37,000
		2	66.80	97.47	36,000
		3	66.24	97.47	36,000
		4	66.47	97.47	36,000
		5	65.87	97.54	36,000
	300	1	63.21	97.65	38,000
		2	60.27	97.73	35,000
		3	65.61	97.54	39,000
		4	63.80	97.66	38,000
		5	63.09	97.80	37,000
	400	1	59.20	97.86	30,000
		2	57.95	97.92	30,000
		3	66.02	97.47	35,000
		4	66.21	97.86	36,000
		5	62.43	97.73	33,000

Table 2. Viscosity, DD(%) and Mw of plasma-treated chitosan in O₂

Gas	Power (W)	Plasma treating time (min)	Viscosity [η]	Degree of deacetylation (DD%)		The molecular weight (Mw) (cal.)
			(exp.)		(cal.)	
O ₂	100	1	110.2		95.43	74,000
		2	86.65		96.62	54,000
		3	84.24		96.62	52,000
		4	84.65		96.55	51,000
		5	73.72		97.14	45,000
	200	1	72.28		96.83	42,000
		2	71.51		97.34	39,000
		3	71.50		97.34	39,000
		4	74.47		97.14	42,000
		5	73.78		97.47	40,000
	300	1	75.50		97.01	43,000
		2	75.50		97.01	43,000
		3	77.46		96.94	44,000
		4	70.84		97.01	39,000
		5	73.84		97.08	42,000
	400	1	81.58		96.68	51,000
		2	73.35		97.01	45,000
		3	74.95		97.01	42,000
		4	60.17		97.79	35,000
		5	62.43		98.05	36,000

obtained using the Mark-Houwink equation (Eq. (4)) [16]. The reduction in molecular weight is evident from the change in viscosity. For the calculation of M_w , the viscosity of the plasma-treated chitosan solution was measured with a Brookfield viscometer (DV-1 prime) with spindle SC4-18 at 25 °C in the range of 30-60 rpm.

$$[\eta] = K \cdot M_w^\alpha \quad (4)$$

Where, M_w : average molecular weight

η : viscosity (cp)

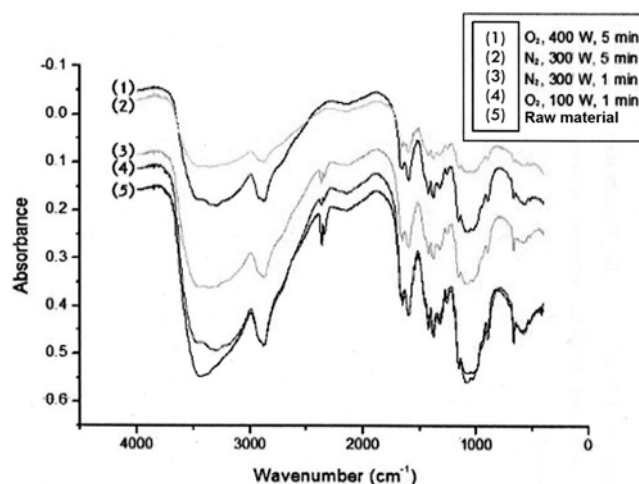
$$K = 1.64 \times 10^{-30} \times (\%DD)^{14} \quad (5)$$

$$\alpha = [-1.02 \times 10^{-2} \times (\%DD)] + 1.82 \quad (6)$$

As shown in Tables 1 and 2, at 100 W the average molecular weight (M_w) decreased from 93,000 of raw chitosan to about 41,000 with plasma-treating time of 5 min in N₂, and 45,000 in O₂ as shown in Table 2; the average molecular weights treated with 300 W and 400 W of PECVD in O₂ were higher than those treated with 100 W and 200 W. This experimental data might mean that too high energy of PECVD rather oxidized the chitosan polymer molecules than breaking the polymer chain.

5. FT-IR Spectrum

In FT-IR analysis [17], the amine (-NH) band was shown at 1,541-1,549 cm⁻¹, the carbonyl (C=O) band at 1,654 cm⁻¹ and 3,422-3,488 cm⁻¹. With increase in the power of PECVD from 100 W to 400 W and with increase in plasma-treating time from 1 min to 5 min, the absorption band peaks substantially decreased. The decrease in band peaks means that the chain of chitosan macromolecules was broken into smaller units, and the size of chitosan molecule became smaller. This FT-IR analysis well agreed with the decrease in viscos-

**Fig. 1. FT-IR spectrum of the plasma-treated chitosan.**

ity as shown above.

CONCLUSIONS

The high molecular weight chitosan shows poor solubility in aqueous solutions, and high viscosity of its solution limits its applications. To improve its solubility and biological, chemical and physical properties, plasma treatment was investigated to prepare low molecular chitosan. The plasma treatment used in this study efficiently depolymerized chitosan in the presence of N₂ and O₂. The molecular weight of chitosan decreased with the increase of the treatment time and with the increase of the PECVD power. The plasma treatment might be a promising technique for the preparation of low

molecular chitosan.

REFERENCES

1. R. A. A. Muzzarelli, *Chitin Handbook*, European Chitin Society, Italy (1997).
2. C. Rodrigues, A. Laranjeira, V. T. de Favere and E. Stadler, *Polymer*, **39**, 5121 (1998).
3. Z. Yan, S. Haijia and T. Tianwei, *Korean J. Chem. Eng.*, **24**, 1047 (2007).
4. S. S. Al-Deyab, M. H. El-Newehy, R. Nirmala, A. A. Abdel-Megeed and H. Y. Kim, *Korean J. Chem., Eng.*, **30**, 422 (2013).
5. K. H. Oudadesse, E. Wers, X. V. Bui, C. Roiland, B. Bureau, I. Akhiyat, A. Mostafa, H. Chaair, H. Benhayoune, J. Fauré and P. Pellen-Mussi, *Korean J. Chem. Eng.*, **30**, 1775 (2013).
6. M. Ul-Islam, N. Shah, J. H. Ha and J. K. Park, *Korean J. Chem. Eng.*, **28**, 1736 (2011).
7. S. Hirano, *Chitin and Chitosan*, Ed. by M. F. A. Goosen, Technomic Publishing Co., Lancaster (1997).
8. C. Zhang, Q. Ping, H. Zhang and J. Shen, *Eur. Polym. J.*, **39**, 1629 (2003).
9. S. S. Kim, Y. M. Lee and C. S. Cho, *Polymer*, **36**, 4497 (1995).
10. D. V. Luyen and V. Rossbach, *J. Appl. Polym. Sci.*, **55**, 679 (1995).
11. N. Kubota, *J. Appl. Polym. Sci.*, **64**, 819 (1997).
12. K. Kurita, K. Tomita, S. Nishimura and K. Shimoda, *J. Polym. Sci. Part A: Polym. Chem. Sci.*, **51**, 2191 (1994).
13. H. J. Kim and D. W. Jeon, *J. Korean Soc. Cloth. Ind.*, **5**, 520 (2003).
14. J. A. Rupley, *Biochem. Biophys. Acta*, **83**, 245 (1964).
15. T. Tanigawa, Y. Tanaka, H. Sashiwa, H. Saimoto and Y. Shigemasa, *Advances in Chitin and Chitosan*, Elsevier, London (1992).
16. P. J. Flory, *Principles of Polymer Chemistry*, Cornell U. Press Ithaca and London (1995).
17. I. F. Amaral, P. L. Granja and M. A. Barbosa, *J. Biomater. Sci. Polymer Ed.*, **16**, 1575 (2005).